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Near infrared light emission quenching in organolanthanide complexes

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We investigate the quenching of the near infrared light emission in Er^{3+} complexes induced by the resonant dipolar interaction between the rare-earth ion and high frequency vibrations of the organic ligand. The nonradiative decay rate of the lanthanide ion is discussed in terms of a continuous medium approximation, which depends only on a few, easily accessible spectroscopic and structural data. The model accounts well for the available experimental results in Er^{3+} complexes, and predicts an $\sim 100\%$ light emission quantum yield in fully halogenated systems. © 2006 American Institute of Physics. [DOI: 10.1063/1.2177431]

The research on low-cost materials emitting in the near infrared (NIR) is receiving a great deal of renewed interest for their potential in local and premise optical communication networks, and imaging and sensing applications. Among these materials, organolanthanides are very promising candidates as they combine the well-established NIR emission properties of Ln^{3+} ions with the unique optical^{1,2} and electrical response³ of organic semiconductors, coupled with their easy processability.

Excitation processes in lanthanide complexes differ considerably from those in inert glasses doped with transition metals. Due to the large absorption cross section of the allowed $\pi-\pi^*$ optical transitions, the organic ligand acts as an efficient light harvester in the ultraviolet-visible spectral window. From the organic photonic antenna the electronic excitations are quickly transferred to the rare-earth ion. The two-step excitation process permits the achievement of a large excited-state population using light fluences four to five orders of magnitude lower than those required for bare ions. Ligands also prevent deleterious formation of metal clusters, allowing the deposition of thin films with Ln^{3+} densities as large as 10^{21} ions/cm³. All these properties make organolanthanides very attracting for the development of low-cost light sources and infrared amplifiers to integrate in planar photonic circuits for optical communications, where light signals can be generated, amplified, and processed.¹⁻⁵

The major drawback of these materials is related to the presence of efficient nonradiative deactivation channels, which shorten the erbium population lifetime from milliseconds to microseconds.^{1,2} NIR emission quenching mainly results from the coupling of the excited state of the Ln^{3+} ion with high frequency vibrations of CH and OH groups.⁶ Substitution of hydrogen with heavier halogen atoms lowers the vibration frequencies and, hence, represents a possible strategy to reduce the induced emission quenching. Investigations on halogenated systems show an unambiguous improvement of the NIR light emission.^{7,8} The best performances have been obtained in perfluorinated (PF) sys-

tems, which show nonradiative decay times in the submillisecond timescale.⁹ NIR emission quantum yield has been drastically enhanced, but remains, however, rather low, around a few percent. Whether these results can be further improved has thus become a central issue, which needs a deeper understanding of the quenching mechanisms in this class of materials. Despite the increasing amount of experimental data available on organolanthanides, a quantitative and predictive model for the relaxation rates of the excited rare-earth ions is still missing.

We discuss a simple approach to describe the nonradiative decay processes in organolanthanides, in which the real molecular structure is replaced by a continuous medium. The model provides a general law for the lanthanide ion nonradiative decay, which rationalizes the existing experimental results on NIR emission quenching in Er complexes, and allows us to assess their ultimate emission performances.

We first discuss the dipolar interaction as the basic mechanism of coupling between the rare-earth ion and the high frequency vibrations of the ligands. The resonant coupling between the transition dipole of the NIR emission and that of the vibrational absorption is described in the framework of Förster's theory of resonance energy transfer.¹⁰ In this model, the transfer rate constant of the excitation from the Er ion (donor) to the ligand vibrations (acceptors) follows a power-law dependence on the dipole-dipole distance r_j :

$$k_{\text{nr}} = k_r \sum_j \left(\frac{R_j}{r_j} \right)^6, \quad (1)$$

where the sum index j runs over all acceptor sites, and k_r is the radiative decay rate constant. R_j represents Förster's distance and is proportional to the overlap integral between the Er emission spectrum normalized to one [$F_D(\lambda)$] and the vibrational absorption cross section [$\sigma_A(\lambda)$] of the quencher (e.g., CH, CF, and CO groups):

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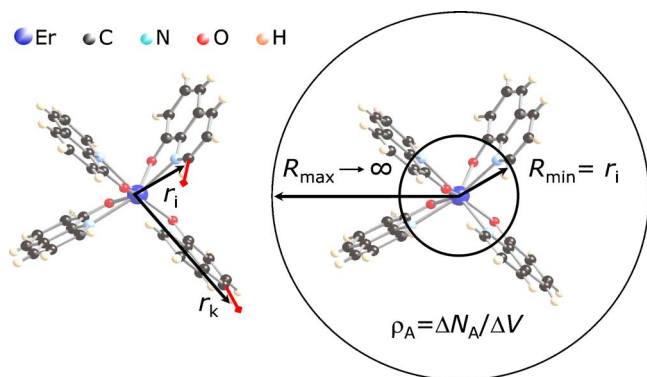


FIG. 1. (Color online) Molecular structure of the Er complex with 8-quinoline (Q), as derived from x-ray diffraction data in Ref. 7 (tetrahedral structure). On the left-hand side, the black arrows display the positions (r_i , r_k) of two (CH) acceptor groups, whose transition dipole moments are pictured as the diamond-head red arrows. In estimating the Er-CH energy transfer rate constant (k_{nr}) in the crystal, the sum is extended to all acceptor sites through Eq. (1) in the text. The CH groups of the nearest neighboring molecules (not shown) are taken into account as well. On the right-hand side, a sphere of radius R_{min} (equal to the minimum Er-acceptor distance r_i) is drawn to indicate the distance above which a constant density of acceptors (ρ_A) is taken for the calculation of k_{nr} using the continuum model.

$$R_j^6 = \frac{9\kappa_j^2}{128\pi^5 n^4} \int F_D(\lambda) \sigma_A(\lambda) \lambda^4 d\lambda. \quad (2)$$

In Eq. (2), n represents the medium refractive index, and κ_j^2 is a geometrical factor, which depends on the relative orientation between the transition dipoles of the Er ion and the j th acceptor. k_r can be evaluated from the Er emission cross section σ_E through the Strickler-Berg law:¹¹

$$k_r = 8\pi n^2 c \int \frac{\sigma_E(\lambda)}{\lambda^4} d\lambda. \quad (3)$$

As the ion deactivation rate constant k_{nr} results from the dipolar interaction with all quenching sites, the estimate of k_{nr} needs a detailed knowledge of the molecular structure, which is, however, unknown in most cases. This impasse can be overcome by replacing the discrete acceptor distribution by a continuous and homogeneous distribution (ρ_A), which represents the average acceptor density, as shown in Fig. 1. In this approximation, k_{nr} reads as¹²

$$k_{nr} = \frac{k_r}{(2\pi n)^4 R_{min}^3} \int F_D(\lambda) \alpha_A(\lambda) \lambda^4 d\lambda \cong \frac{\lambda_{em}^4}{(2\pi n)^4} \frac{k_r \langle \alpha_A \rangle_{Er}}{R_{min}^3}, \quad (4)$$

where R_{min} is the minimum distance between the lanthanide ion and acceptors, below which $\rho_A=0$; κ_j^2 is averaged over all dipole directions, which yields $\langle \kappa_j^2 \rangle = 2/3$; $\alpha_A = \sigma_A \rho_A$ is the vibrational absorption coefficient of either the rare-earth complex crystal or the matrix in which the lanthanide ions are dispersed. Notably, k_{nr} depends on two spectroscopic quantities only: the radiative NIR emission rate constant k_r and $\langle \alpha_A \rangle_{Er}$, the vibrational absorption averaged over the erbium emission spectral window, peaked at $\lambda_{em} = 1530$ nm. The structural information is limited to the knowledge of R_{min} , an estimate of which can be provided by simple chemical and geometrical considerations.⁶

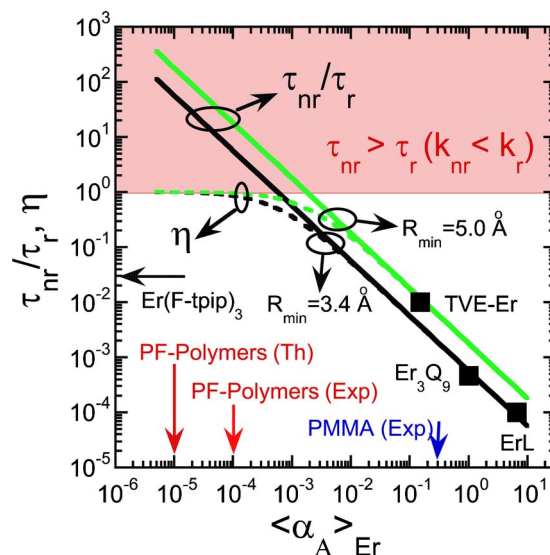


FIG. 2. (Color online) Nonradiative lifetime τ_{nr} , normalized to the radiative time constant $\tau_r = 5$ ms, and quantum yield $\eta = \tau_{nr}/(\tau_r + \tau_{nr})$ as a function of the vibrational absorption averaged over the Er emission spectrum, $\langle \alpha_A \rangle_{Er}$ (cm^{-1}). The two continuous (dashed) lines show the τ_{nr}/τ_r (η) curves calculated through the continuum model with $R_{min} = 3.4$ and 5 Å, respectively. The experimental values of τ_{nr}/τ_r are plotted as the solid squares. The vertical arrows show the theoretical (Th) (Ref. 20) and experimental (Exp) (Ref. 19) values of $\langle \alpha_A \rangle_{Er}$ of perfluorinated (PF) polymers and polymethylmethacrylate (PMMA) (Ref. 16). The horizontal arrow shows the experimental values of τ_{nr}/τ_r and η of the perfluorinated complex $\text{Er}(\text{F-tpip})_3$ (Ref. 9).

In order to test the validity of the continuum approximation, the nonradiative decay rate constant calculated by using Eq. (4) has been compared with that obtained accounting for the real donor-to-acceptor distances through Eq. (1). We have performed this analysis in Er-quinoline complexes, for which detailed x-ray studies have been reported.^{7,13} The comparative study confirms that Eq. (4) just leads to a negligible underestimation, $\sim 10\%$, of the exact dipole-induced transfer rate, calculated using Eq. (1). The reason why the continuum approximation works so well ultimately stems from the relatively large value of R_{min} (~ 3.4 Å), which permits a continuous-like packing of hydrogen atoms. As this latter consideration holds for most organolanthanides, modeling the real molecular structure with a continuous medium is expected to provide a reliable estimate of the light emission quenching caused by dipolar interaction for the whole class of rare-earth complexes, including systems with lanthanide ions different from erbium.

In the following, we examine some experimental results, summarized in Fig. 2, of archetypal of the NIR emission properties of Er complexes. Finally, at the light of the continuum model we discuss the potential of halogenated complexes as efficient NIR emitters.

The nonradiative lifetimes of unsubstituted Er complexes fall in the sub- and microsecond timescales ($0.5 - 3$ μs).^{1-3,7,13} The shorter decays (< 1 μs) are due to the presence of OH groups within the coordination sphere of the lanthanide ion.² The scattering of the τ_{nr} experimental data is also related to the dependence of τ_r and $\langle \alpha_A \rangle_{Er}$ on the specific ligand and the actual molecular structure.¹⁴ A quantitative estimate of τ_{nr} in the continuum model can be made for

m-terphenyl-based (L) Er^{3+} complexes (ErL) and Er-8-hydroxyquinoline (Er_3Q_9) in the solid state, for which the necessary optical and structural data are available. In ErL , $\tau_r = 1/k_r = 4$ ms,² $R_{\min} = 3.7$ Å, and $\langle\alpha_A\rangle_{\text{Er}} \sim 6.6$ cm⁻¹;^{15,16} assuming a refraction index $n \sim 1.5$, the continuum model yields $\tau_{\text{nr}} = 1/k_{\text{nr}} \sim 0.4$ μs, in good agreement with the measured NIR lifetime, 0.5 μs.² In Er_3Q_9 , $\tau_r = 5 \pm 0.5$ ms,¹⁷ $R_{\min} = 3.4$ Å,¹³ and $\langle\alpha_A\rangle_{\text{Er}} = 1 \pm 0.3$ cm⁻¹.¹⁸ With these parameters and for $n \sim 1.5$, the theoretical nonradiative lifetime becomes $\tau_{\text{nr}} \sim 2.6$ μs, in very good agreement with the experimental emission lifetime, 2.3 μs.¹³

As predicted by the continuum model, the previous analysis shows that the larger the vibrational absorption at 1530 nm, the faster the nonradiative decay rate of the rare-earth complexes. A further elegant proof of this scaling law is provided by Van Deun's experimental results in solutions of complexes synthesized with the same mononuclear molecular structure, namely, Er-8-quinoline (ErQ), Er-5-chloro-Q (Er5ClQ), and Er-5,7-dichloro-Q (Er57ClQ).⁷ In these systems, the Cl contribution to $\langle\alpha_A\rangle_{\text{Er}}$ is negligible, owing to the heavy mass of the halogen atom.⁶ Neglecting the contribution of the solvent, $\langle\alpha_A\rangle_{\text{Er}}$ is proportional to the density of CH groups, and, hence, to the number N_{H} of hydrogen per each quinoline. Therefore, according to Eq. (4), both the decay time (τ_{nr}) and the NIR emission quantum yield ($\eta \sim \tau_{\text{nr}}/\tau_r$) scale as $1/N_{\text{H}}$, i.e., $\tau_{\text{nr}}(\text{ErQ}) : \tau_{\text{nr}}(\text{Er5ClQ}) : \tau_{\text{nr}}(\text{Er57ClQ}) = \eta(\text{ErQ}) : \eta(\text{Er5ClQ}) : \eta(\text{Er57ClQ}) = 1/6 : 1/5 : 1/4 = 1 : 1.2 : 1.5$, in good agreement with the observed experimental values, 1:1.07:1.53 for τ_{nr} and 1:1.22:1.54 for η .

Equation (4) indicates the potential strategies for designing molecular systems with improved NIR emission efficiency. Brighter phosphorescence can be obtained by increasing the minimum distance R_{\min} between the lanthanide ion and the quenchers. However, for an efficient radiative emission ($k_{\text{nr}} \leq k_r$), R_{\min} should be larger than 30 Å (assuming $\langle\alpha_A\rangle_{\text{Er}} \sim 1$ cm⁻¹). This distance is much larger than the typical size of organolanthanide molecules; thus, simply acting on the Er^{3+} -CH distance appears inadequate to completely suppress the nonradiative decay pathway. An important step towards the achievement of this objective can be made by reducing the vibrational absorption $\langle\alpha_A\rangle_{\text{Er}} = \langle\sigma_A\rangle_{\text{Er}}\rho_A$. This approach requires the synthesis of molecules with a smaller vibrational cross section $\langle\sigma_A\rangle_{\text{Er}}$ (achievable, e.g., by using halogenated ligands), and possibly, with a lower density of vibrational quenching groups ρ_A . The maximum vibrational absorption $\langle\sigma_A\rangle_{\text{max}}$ allowed for an efficient radiative NIR emission ($k_{\text{nr}} \leq k_r$) can be assessed in the framework of the continuum model; from Eq. (4), we obtain $\langle\sigma_A\rangle_{\text{max}} = (2\pi n)^4 R_{\min}^3 / \lambda_{\text{em}}^4 = 5 \times 10^{-4}$ cm⁻¹, a value three orders of magnitude smaller than the one measured in unsubstituted systems. Optical loss measurements in perfluorinated plastic fibers show an attenuation near 1530 nm as small as $\approx 1 \times 10^{-4}$ cm⁻¹, including Rayleigh scattering,¹⁹ and much smaller than $\langle\sigma_A\rangle_{\text{max}}$. The vibrational contribution to the optical loss spectrum has been theoretically calculated in various fully fluorinated polymers, namely, Teflon-AF, Cytop, and perfluorocyclobutyl (PFCB).²⁰ In these systems, the ab-

sorption near 1530 nm amounts to less than 10^{-5} cm⁻¹. Even more favorable conditions are expected in chlorinated organolanthanides, due to the heavier mass of Cl atoms. All these data lead to the conclusion that ample margins exist for halogenated erbium complexes to provide a bright NIR emission.

In light of these considerations, we can finally comment on the recent results on fluorinated complexes. NIR emission lifetimes as long as 50 μs have been observed in a partially fluorinated system, namely, 1,1,1-tris(4-trifluorovinyloxy) phenylethane (TVE)-based polymer doped with Er^{3+} (TVE-Er).^{8,20} In this system, $\langle\alpha_A\rangle_{\text{Er}} \sim 0.15$ cm⁻¹, while R_{\min} is expected to be ~ 4 –5 Å. With these parameters, the continuum model yields a nonradiative lifetime $\tau_{\text{nr}} \sim 30$ –60 μs, in reasonable agreement with the experimental finding. In a fully fluorinated Er complex in the solid state, $\text{Er}(\text{F-tpi})_3$,⁹ an increase in luminescence decay time up to 220 μs has been observed; however, this value is still much shorter than the radiative Er lifetime. Assuming that fluorination mainly affects α_A , from the observed 220 μs time constant we estimate a residual $\langle\alpha_A\rangle_{\text{Er}} \sim 1 \times 10^{-2}$ cm⁻¹. Such absorption is much higher than both the NIR optical losses measured in perfluorinated plastic fibers and theoretical assessments. These considerations suggest that the observed low emission quantum yield is due to excited-state energy transfer towards quenching centers (solvent molecules or reaction residues containing hydrogen or deuterium atoms), possibly assisted by the fast Er-Er migration and favored by the long dipole-dipole interaction length.

In conclusion, we have provided a comprehensive analysis of the near infrared emission quenching in erbium complexes. In the continuum approximation, the erbium-to-ligand transfer rate can be assessed from the measurements of the vibrational absorption spectrum of the complex, the lanthanide radiative lifetime, and the minimum distance between the rare-earth ion and the quenchers. The continuum model shows that the nonradiative lifetime of excited Er ions falls in the microsecond timescale if coupled to CH vibrations. For achieving an efficient near infrared emission, the Er complex must feature a mean vibrational absorption lower than 5×10^{-4} cm⁻¹ across the erbium emission spectrum. Spectroscopic data on state-of-the-art perfluorinated polymers satisfy very well this stringent requirement, providing a renewed stimulus for the development of highly efficient halogenated organolanthanides for near infrared photonic devices.

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- ¹⁵The vibrational absorption $\langle \alpha_A \rangle_{Er}$ has been extracted from the optical loss spectrum of a polymethylmethacrylate (PMMA) layer doped with 10% Nd^{3+} complexes (NdL) (G. Hebbink, Ph.D. thesis, Twente University, 2002), for which no lanthanide emission occurs near 1530 nm, and thus $\langle \alpha_A \rangle_{Er} = \langle \alpha_{NdL} \rangle_{Er}$. The contribution $\langle \alpha_{NdL} \rangle_{Er}$ to the vibrational absorption of the blend, $\langle \alpha_{PMMA:NdL} \rangle_{Er}$, has in turn been assessed from the relation $\langle \alpha_{PMMA:NdL} \rangle_{Er} = x \langle \alpha_{NdL} \rangle_{Er} + (1-x) \langle \alpha_{PMMA} \rangle_{Er}$ ($x=0.1$), using the experimental values $\langle \alpha_{PMMA:NdL} \rangle_{Er} \sim 0.9 \text{ cm}^{-1}$ and $\langle \alpha_{PMMA} \rangle_{Er} \sim 0.3 \text{ cm}^{-1}$ (Ref. 16).
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